Screening of organic solvents for selective extraction of n-butanol from aqueous solution using molecular dynamics simulations

Dissertation submitted to
Visvesvaraya National Institute of Technology, Nagpur
in partial fulfillment of the requirements for the award of
the degree Chemical Engineering

Master of Technology
in
Chemical Engineering

by

Vishesh A Velani (MT23MCL001)

under the guidance of

Dr. Piyush P. Wanjari

Department of Chemical Engineering
Visvesvaraya National Institute of Technology
Nagpur 440 010 (India)

2024-25

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Declaration

I, **Vishesh A Velani**, hereby declare that this dissertation titled **"Screening of organic solvents for selective extraction of n-butanol from aqueous solution using molecular dynamics simulations"** is carried out by me in the Department of Chemical Engineering of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier whole or in part for the award of any degree/diploma at this or any other Institution / University.

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This to certify that the dissertation titled "Screening of organic solvents for selective extraction of n-butanol from aqueous solution using molecular dynamics simulations" is submitted by **Vishesh A Velani (MT23MCL001)** in partial fulfillment of the requirements for the award of the degree of **Master of Technology in Chemical Engineering**, VNIT Nagpur. The work is comprehensive, complete and fit for final evaluation.

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Abstract

N-butanol is a renewable, energy dense and high-octane biofuel that demands efficient separation from the aqueous solution during its synthesis by fermentation, hydroformylation, hydrogenation and many other approaches. Liquid-liquid extraction is a promising method that can be used to isolate n-butanol from aqueous solution even at extremely lower concentrations. In this study, we perform molecular dynamics (MD) simulations using five organic solvents, namely, benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, 4-n-butylphenol and n-decanol to investigate their extraction efficiency towards n-butanol from water. Our results demonstrate oleyl alcohol as the most effective solvent that capture the highest 98.42% n-butanol, among all the five extractants used with varying concentrations between 50 to 300 ml/l. The changes in capturing efficiencies of extractants are significantly attributed to their molecular structures. Oleyl alcohol shows highest capture due to its long chain, but a slight bent structure in aqueous media that has been verified through its non-trans dihedral angle distribution near its either side of the double bond. N-decanol, on the other hand, despite having the long-chain, extracts least n-butanol especially at higher concentrations due to its trans-dominated straight-chain conformation. Next studies performed by altering n-butanol concentration from 10 to 50 g/l again shows comparatively better n-butanol capture by oleyl alcohol especially at $\leq$ 30 g/l concentrations. The hydrogen bond calculation between butanol-extractant, extractant-water and butanol-water depicts dominant nature of extractant-water interactions for determining the overall capture for most solvents including oleyl alcohol. It has been observed that multiple factors such as the shape and size of the extractants, hydrogen bonding between extractant, butanol and water, concentrations of n-butanol and extractants as well as the temperature decide the ultimate fate of the capture.

Keywords

n-butanol extraction, molecular dynamics simulation, oleyl alcohol, biofuel separation, liquid-liquid extraction, solvents screening

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NOMENCLATURE

MDS	Molecular Dynamics Simulation
GAFF	General AMBER Force Field
GROMACS	Groningen Machine for Chemical Simulations
TIP4P	Transferable Intermolecular Potential with 4 Points
VMD	Visual Molecular Dynamics
PDB	Protein Data Bank (file format for 3D molecular structure)
.gro	GROMACS structure file
.top	GROMACS topology file
.xvg	Graphing file format used by GROMACS
.prmtop	AMBER parameter/topology file
.inpcrd	AMBER initial coordinate file
NVT	Canonical Ensemble (Constant Number, V &T)
Antechamber	Tool in AMBER for assigning atom types and charges
LEaP	AMBER tool for building & editing molecular systems
Packmol	Tool for packing molecules into a simulation box
Dihedral angle	Angle between 2 intersecting planes formed by 4 atoms
GAMESS	General Atomic and Molecular Electronic Structure System
AM1-BCC	Austin Model 1 with Bond Charge Corrections
TIP4P-Ew	Four-site water model with Ewald summation
NPT Ensemble	Constant Number of particles, Pressure, and Temperature ensemble
PME	Particle Mesh Ewald (Method for Long-Range Electrostatics)
gmx hbond	GROMACS tool to calculate hydrogen bonds
NRTL, UNIQUAC, COSMO-SAC	Thermodynamic models for phase equilibrium calculations

1. Introduction

1.1 Background

The rising global need for clean and renewable energy sources has sparked growing interest in fuels derived from biological processes, particularly amid increasing concerns over climate change and the decline of fossil fuel reserves[1]. Among the various biofuel options, n-butanol has appeared as a highly promising alternative due to its high energy density, high octane number, lower volatility, superior blending ability with gasoline, and enhanced drop-in fuel performance when compared to ethanol[2–6]. While it was originally produced via the acetone-butanol-ethanol fermentation process, n-butanol is now gaining renewed attention, not only as a sustainable fuel but also as a versatile industrial chemical[7–11] . However, the small concentration of n-butanol produced during the fermentation process significantly restricts its isolation from the aqueous solution[7,12–14]. This highlights the critical need for effective and energy-efficient n-butanol separation technologies.

The efficiency of solvent extraction depends heavily on the choice of solvent. Solvents such as Decanol, Benzyl Benzoate, Oleyl Alcohol, and Ethyl Butyrate have shown promise due to their high partition coefficients, low water solubility, and minimal toxicity to microbial systems. Despite this, the mechanisms that drive the interactions between n-butanol and these solvents remain poorly understood at the molecular level [15,16]. Common separation techniques namely, distillation, gas stripping, adsorption, and membrane-based methods have been widely explored[17–20]. Still, they often fall short when dealing with dilute aqueous systems, due to high energy requirements, excessive costs, or operational complexity[21–25]. Liquid-liquid extraction (LLE) offers a promising and energy-efficient alternative for recovering butanol, especially under milder operating conditions[8,15,26,27] . The key to making LLE work lies in choosing the right solvent that can selectively pull-out n-butanol while being safe and staying separate from water. The solvents such as decanol, benzyl benzoate, oleyl alcohol, and 2-ethyl-1-hexanol, have shown strong potential due to their high partitioning ability and selective extraction performance[9,28–31]. Still, the understanding of the precise molecular mechanisms that make these solvents effective is lacking[32–34]. Gaining insight into these fundamental interactions is critical for advancing the design of more efficient, targeted solvent systems for sustainable butanol recovery.

The current study uses MD simulations to evaluate the performance of five organic solvents - decanol, benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, and 4-n-butylphenol - in extracting n-butanol from water. Using the GROMACS simulation package, we examine how variations in butanol and extractant concentrations influence the n-butanol capture efficiency and intermolecular interactions such as hydrogen bonding. This research focuses specifically on utilizing extractant with binary n-butanol–water systems, as they reflect the core thermodynamic environment in continuous extraction processes, particularly those integrated with microbial fermentation[30,32,35]. By building on earlier experimental and theoretical findings[9,28,29,35–37], this study

delivers new molecular-level insights to inform the selection and design of solvents. The ultimate goal is to support the development of efficient, scalable, and environmentally sustainable butanol recovery processes[30,31,38,39].

1.2 Problem Statement

The n-butanol, which is recovered from various sources like aqueous solution or fermentation broth, remains a significant challenge in biofuel production because it is not very concentrated and mixes easily with water. Getting n-butanol back from fermentation broth or aqueous solution is still a big problem in the production of biofuels. In various ABE fermentation processes, n-butanol concentrations are < 30 % by weight, making its separation energy-intensive and economically unsustainable with conventional techniques like distillation. Solvent extraction may be an efficient process for the separation of n-butanol, but it cannot be made better because we don't fully understand how the molecules of liquids like n-butanol and the solvent interact with each other. To improve the process and lower the costs of the extraction process by using liquid-liquid extraction, more study needs to be done on the solvent to find out the effect of the concentration and how it captures n-butanol at various concentrations.

1.3 Objectives

There are the following objectives of research:

1. To determine the efficiency of five organic solvents—Decanol, Benzyl Benzoate, Oleyl Alcohol, 2-Ethyl-1-Hexanol, 4-n-Butylphenol in extracting butanol from aqueous solution using molecular dynamics simulations.
2. To analyze the molecular mechanisms of solvent–solute interactions using the MDS, with a main focus on hydrogen bonding and solvation behavior
3. To investigate the effects of varying solvent and n-butanol concentrations on extraction efficiency and capture dynamics.
4. To provide insights that can inform the development of optimized, cost-effective solvent-based recovery methods for n-butanol in biofuel production systems.

1.4 Scope of study

This research conducts molecular-level analysis of n-butanol selective extraction from aqueous solutions using different organic solvents to advance bio-butanol recovery technology. The research utilizes molecular dynamics simulations to investigate the capture efficiency and hydrogen bond formation of benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, 4-n-butylphenol, and decanol when exposed to different concentrations of solute and solvent at various temperature levels.

Research focuses on studying solvent–solute and solvent–water interactions to establish the structural and thermodynamic principles that enable selective extraction. The research examines the effects of solvent polarity along with molecular flexibility and functional group availability on butanol recovery and hydrogen bond disruption. The simulation process maintains constant solvent concentrations while adjusting butanol levels and testing different temperature settings to replicate real fermentation conditions and aqueous solution environments.

This work exceeds conventional equilibrium analysis through its use of hydrogen bond metrics and Dihedral angle measurements of both oleyl alcohol and decanol which together deliver a full understanding of extraction efficiency. The study findings assist researchers in determining effective solvent choices and molecular solvent design for sustainable n-butanol recovery across multiple biorefinery uses.

2. Literature review

Numerous studies have focused on the extraction process of n-butanol from fermentation broth. Research on organic solvents and computational methods has become increasingly significant in scientific investigations. This section analyses major discoveries about solvent-based extraction methods and examines their significance. Molecular dynamics simulations have proven valuable for both comprehension and enhancement of these fermentation processes. The recovery of n-butanol from aqueous solutions is a critical stage in the biofuel production and purification procedures. Conventional separation processes (distillation etc.) may tend to be energy consuming and ineffective because of azeotropy behaviour of butanol/water solutions. Hence, other methods such as liquid–liquid extraction (LLE) have also gained attention in having better physical separation performance in addition to the reduced energy consumption.

Recent advances in computational techniques such as molecular dynamics (MD) simulations have opened up new avenues for understanding the solvent behaviour at the molecular level[36,40,41]. Previous investigations have shown that solvent properties such as its hydrophobicity, molecular geometry, and hydrogen-bonding ability can significantly influence its n-butanol extraction efficiency[40,42–46]. Complementing these insights, predictive models like COSMO-RS, UNIFAC, MOSCED, and CAMD have been employed to guide the screening and design of suitable solvents[29,47–51]. Although ionic liquids (ILs) have demonstrated strong potential in butanol extraction due to their unique physicochemical properties, their practical application stays limited by factors such as high production costs, toxicity concerns, and difficulties in downstream separation[33,52]. These constraints underscore the importance of identifying alternative solvents that are not only effective but also economically and environmentally sustainable. In this context, computational methods provide a valuable framework for systematically evaluating a broad range of organic solvents with potential for industrial application.

2.1 Solvent Selection and Extraction Efficiency

The performance of LLE is highly related to the type of solvent. The applicability of n-butanol, for use as solvent and extractant, was demonstrated for organics and inorganics in this context (Reetz and König, 2021), which underlines the synergies, which can be exploited, due to the fact that it suits for emulsions breaking and for separation of polar compounds from aqueous layers. According to their work, the influence of solvent polarity and hydrophobicity was significant in the extraction efficiency[53].

2.2 Molecular Dynamics Simulations in Solvent Analysis

Molecular dynamics has become a valuable way to explore the microscopic interactions involving solvents and solutes. Macchiagodena et al. (2022) used MD simulations and the small angle X-ray scattering and wide-angle X-ray scattering measurements to investigate 2-butanol aqueous solutions. It appeared that 2-

butanol is prone to a complete aggregation at concentrations higher than 1 M, drastically affecting the characteristics of the solution[54].

2.3 Hydrogen Bonding and Solvent-Solute Interactions

Hydrogen bonding is an important contribution to the extraction mechanism. The number and strength of hydrogen bonds among butanol, water and solvent are considered to influence the separation of butanol. It has been reported that solvents that are capable of breaking the hydrogen bonds present in butanol-water lead to better extraction. For example, some solvents may preferentially be able to hydrogen bond with butanol, thereby decreasing its affinity for water, and increasing its extraction to the organic phase[55].

2.4 Gaps in Current Research

However, there are critical questions that must be addressed to advance these solvent-based n-butanol recovery techniques. A striking deficiency is the dearth of comparative studies benchmarking multiple solvents in single experimental or simulation settings. Many studies in the literature deal with single solvents, and relative comparisons are difficult. Moreover, the molecular-level factors that determine solvent selectivity and efficiency are poorly understood. Furthermore, computational methods such as molecular dynamics simulations provide some, but limited, insights which are highly underused in relation to experimental validation, resulting in a gap in translational relevance and applicability.

2.5 Significance of This Study

This paper proposes to address these weaknesses by a systematic and holistic analysis. In this study, five organic solvents, namely, Decanol, Benzyl Benzoate, Oleyl Alcohol, 2-Ethyl-1-Hexanol, 4n-Butylphenol under uniform simulated conditions are assessed for a comparison of their effectiveness to recover n-butanol. Using molecular dynamics simulations, in this work the molecular details of the interactions between n-butanol and the solvents are studied in some detail with a special emphasis on hydrogen bonding, solvent clustering, determining the dihedral angles and also the impact of the shape and size of the molecule on the capture efficiency. The results provide comparative information about performance of the solvents at different butanol concentrations and thermal conditions, in support of rational selection of efficient and sustainable extractants. Finally, by linking our computational analysis to theory the present study also supplies fundamental insight to be used in experimental investigations and commercial scale separation processes for bio-butanol retrieval.

3. Methodology

3.1 Solvent Selection and Force Field Parameterization

This study employs molecular dynamics simulations to evaluate the efficiency of five organic solvents, namely, benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, 4-n-butylphenol, and n-decanol in selectively extracting n-butanol from aqueous systems. Initially, all the organic molecules used in our simulations were parameterized by Generalized Amber Force Field (GAFF)[56]. The molecular structures of n-butanol and the five extractants were optimized using GAMESS 2023 R1 with the Hartree-Fock method and 6-31G(d) basis set to ensure minimized geometries[57,58]. The output log files were converted into XYZ coordinate files using Gabedit (version: 2.5.1, July 27, 2021, stable version) and further transformed into PDB files via Open Babel (Obabel, version: 3.1.1, released on February 8, 2023).

3.2 Charge Assignment and System Preparation

These optimized structures were further processed using antechamber module in AmberTools 22 package for assigning partial atomic charges using AM1-BCC method[59]. The water molecule used in our simulations was parameterized using TIP4P-Ew potential[60]. The mol2 files were generated for each molecule. These files were loaded into xLeap to create library (.lib) files with manually adjusted charges for neutrality. The solvent-solute mixtures were constructed using Packmol (version: 18.169) by specifying solvent-to-solute ratios to mimic varying extraction conditions. The prepared systems were solvated with water in a cubic simulation box of dimensions 75×75×75, ensuring realistic aqueous environments. The topology (.prmtop) and coordinate (.inpcrd) files generated in xLeap were converted into GROMACS-compatible formats (.gro and .top) using amb2gro.

3.3 Molecular Dynamics Simulation Setup

The Molecular Dynamic simulations were performed using GROMACS 2022.5 simulation engine[61]. Our typical simulation system consisted of 10000 water molecules with 73 n-butanol molecules for the systems having 30 g/l n-butanol concentration and 94 benzyl benzoate molecules for the systems having 100 ml/L benzyl benzoate concentration. In this research, the composition that I have used for the simulation is given below in detailed in Table 1. It is used to determine the effect of extractant concentration on *n*-butanol extraction efficiency by varying the concentration of the extractant for each of the five organic solvents i.e. *n*-decanol, benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, and 4-*n*-butylphenol were the simulations were conducted by varying the concentration across a range of 50 to 300 ml/l, while the concentration of *n*-butanol is maintaining constant at 30 g/l (73 molecules). These system compositions allowed us to determine systematic evaluation of how solvent loading influences molecular interactions and butanol capture behavior under various aqueous conditions.

Table 3.1
Simulation System Composition for *n*-Butanol Extraction Using Five Organic Solvents at Varying Extractant Concentrations.

Table 3.1 (a)

System Composition for n-Butanol + n-Decanol Simulations at Varying Extractant Concentrations. Number of extractant molecules and constant n-butanol concentration (30 g/L, 73 molecules) for extractant concentrations ranging from 50 to 300 mL/L.

System	extractant concentration (ml/l)	extractant molecules	n-butanol concentration (g/l) and molecules
Butanol-Decanol	50	47	30 and 73
	100	94	30 and 73
	150	141	30 and 73
	200	188	30 and 73
	250	235	30 and 73
	300	282	30 and 73

Table 3.1 (b)

System Composition for n-Butanol + Benzyl Benzoate Simulations at Varying Extractant Concentrations. Details of benzyl benzoate molecule counts corresponding to extractant concentrations (50–300 mL/L) and fixed n-butanol composition.

System	extractant concentration (ml/l)	extractant molecules	n-butanol concentration (g/l) and molecules
Butanol - Benzyl Benzoate	50	48	30 and 73
	100	95	30 and 73
	150	143	30 and 73
	200	190	30 and 73
	250	238	30 and 73
	300	285	30 and 73

Table 3.1 (c)

System Composition for n-Butanol + Oleyl Alcohol Simulations at Varying Extractant Concentrations. List of oleyl alcohol molecules across six concentrations with a constant n-butanol concentration.

System	extractant concentration (ml/l)	extractant molecules	n-butanol concentration (g/l) and molecules
Butanol – Oleyl Alcohol	50	30	30 and 73
	100	59	30 and 73
	150	89	30 and 73
	200	118	30 and 73
	250	148	30 and 73
	300	177	30 and 73

Table 3.1 (d)

System Composition for n-Butanol + 2-Ethyl-1-Hexanol Simulations at Varying Extractant Concentrations. Simulation setup describing extractant molecule numbers for 2-ethyl-1-hexanol at fixed n-butanol concentration (30 g/L).

System	extractant concentration (ml/l)	extractant molecules	n-butanol concentration (g/l) and molecules
Butanol – 2-ethyl-1-hexanol	50	77	30 and 73
	100	155	30 and 73
	150	232	30 and 73
	200	310	30 and 73
	250	387	30 and 73
	300	465	30 and 73

Table 3.1 (e)

System Composition for n-Butanol + 4-n-Butylphenol Simulations at Varying Extractant Concentrations. Corresponding molecule counts for 4-n-butylphenol in the simulation box with 73 n-butanol molecules.

System	extractant concentration (ml/l)	extractant molecules	n-butanol concentration (g/l) and molecules
Butanol - 4-n-butylphenol	50	60	30 and 73
	100	120	30 and 73
	150	180	30 and 73
	200	240	30 and 73
	250	300	30 and 73
	300	360	30 and 73

The first stage involved energy minimization using the steepest descent algorithm until convergence criteria were met. This was followed by an equilibration run of 20 ns at the 300 K temperature using V-rescale temperature coupling and at the 1 bar pressure using the Berendsen barostat. Finally, production runs were conducted for another 20 ns in an NPT ensemble to calculate the statistics of the properties of interest, by keeping temperature at the 300 K with the Nose-Hoover thermostat and pressure at the 1 bar using C-rescale barostat. The 2 fs timestep was used for integrating the equations of motion and the system coordinates were saved every 1ps. Production runs were conducted over three stages (PRD1, PRD2, PRD3), each lasting 10 ns with a time step of 2 fs. Non-bonded interactions were calculated with a cutoff radius of 1.0 nm for van der Waals and Coulomb interactions, while long-range electrostatics were treated using the Particle Mesh Ewald method. Periodic boundary conditions were applied throughout all simulations. The short-range non-bonded interaction energies were calculated using 1 nm cutoff for both coulombic and van der Waals forces, while long-range electrostatic interactions were evaluated by particle mesh Ewald method[62]. Long-range van der Waals corrections were also implemented to account for the dispersion forces.

3.4 Capture Efficiency Analysis

The post-simulation analysis was conducted to evaluate the efficiency of solvent systems in capturing n-butanol molecules and their hydrogen bonding interactions. A Python-based script was developed to quantify the number of n-butanol molecules captured by the solvent, employing a distance-based threshold approach. Additionally, hydrogen bond analysis was performed to determine the strength and dynamics of interactions between n-butanol, solvents, and water molecules at various simulation stages.

The Python script utilized the GROMACS trajectory files (prd*.gro and prd*.xtc) to calculate pairwise distances between all atoms of n-butanol and solvent molecules (e.g., Decanol or Benzyl Benzoate etc). Using a predefined threshold distance of 5.0 Å, the script identified n-butanol molecules considered "captured" by the solvent. For each frame of the trajectory, the number of captured molecules was recorded along with the total number of atoms in the system. The results were written to an output file (1captured_molecules_with_atom_count.txt), which also included the average number of captured molecules over all frames. This analysis provided a quantitative measure of solvent efficiency in capturing n-butanol under varying conditions.

3.5 Hydrogen Bond Analysis

Hydrogen bond analysis was conducted using GROMACS tools (gmx HBond). Hydrogen bonds were defined based on the donor-acceptor distance cutoff of the3.5 Å and the hydrogen-donor-acceptor angle cutoff of 30°. The analysis focused on three key interactions: water-n-butanol, solvent-n-butanol, and water-solvent pairs across simulation stages (EQM, PRD1, PRD2, PRD3). Data from this analysis provided insights into solute-solvent interaction strength and stability.

3.6 Dihedral Angle Analysis

In addition to hydrogen bonding analysis, dihedral angle distributions also were investigated to study conformational flexibility of the solvent molecules and their contribution to butanol interaction kinetics. Dihedral angle analysis was done by employing the GROMACS utility gmx_mpi angle with the -type dihedral flag. For a typical solvent system, a typical dihedral was selected along the alkyl chain (except hydroxyl termini) to identify torsional freedom and structural stability in butanol interaction. To create the index file the python script was used An index file was prepared defining atom quartets that form the torsional angles of interest. The tool was executed on the trajectory files (prd*.xtc), and dihedral angle values were calculated on all frames of the production runs. The resulting angular distributions were plotted to monitor conformational preferences under simulation conditions. These profiles helped to identify whether specific solvent orientations were associated with enhanced butanol capture or hydrogen bonding. The analysis was particularly useful in describing branched (e.g., Oleyl Alcohol) vs. linear (e.g., decanol)

solvent system differences, with additional insight into the structure–function relationship in solvent behavior.

Overall, this simulation technique determines a comprehensive analysis of solute–solvent behavior at molecular level. The integration of force field-based parameterization, trajectory analysis, and customized scripting provided a holistic strategy for evaluating both static and dynamic properties relevant to n-butanol extraction. Capture efficiency, hydrogen bonding architectures, and dihedral angle distributions were investigated to define key correlations between extraction efficiency and solvent structure. By employing consistency in simulation protocols for all solvent systems, this protocol enables comparative conclusions to be valid and extensible as well as offers a firm basis for future experimental validation and industrial optimization protocols.

4. Results and discussion

4.1 Butanol Capture Efficiency as a Function of Extractant Concentration

The preliminary MD simulations conducted using five different organic extractants, namely, benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, 4-n-butylphenol and n-decanol were first analyzed to evaluate their n-butanol capture capacity from the aqueous solution (Figure 4.1). The efficiency of n-butanol capture was assessed for all the five extractants as a function of extractant concentration ranging from 50 to 300 ml/l by considering n-butanol concentration of 30 g/l. The capture efficiency was determined based on the percentage of n-butanol molecules that remained within 5 Å of the extractant molecules out of the total n-butanol molecules used within the system.

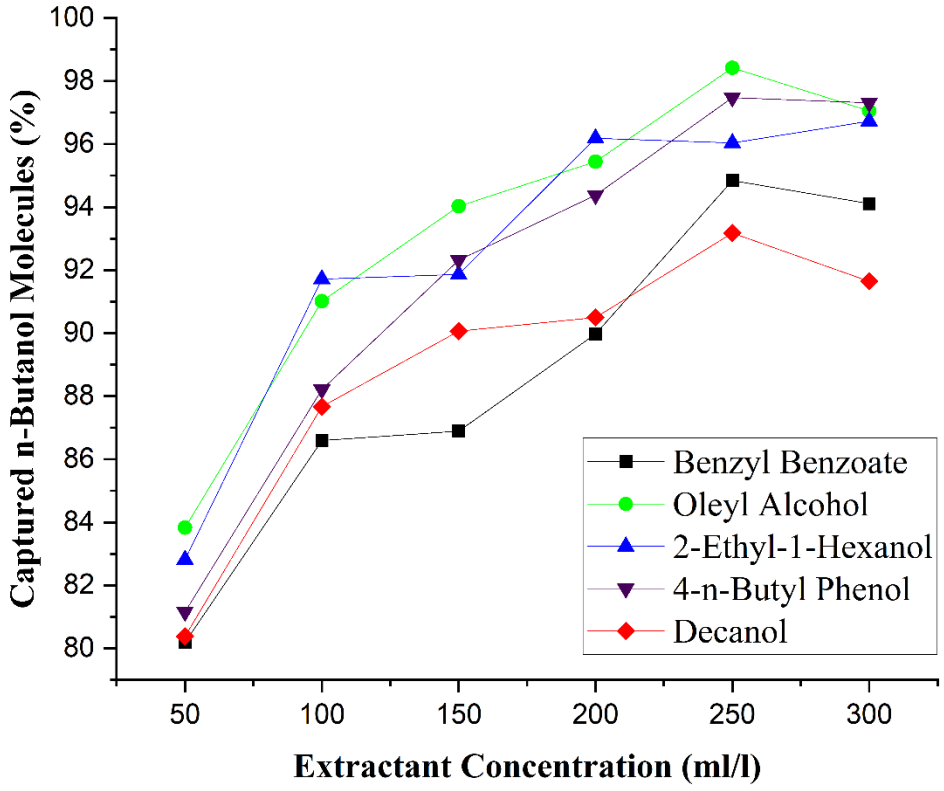


Fig. 4.1. Percent captured n-butanol molecules as a function of concentration for five organic extractants. The capture efficiency is determined based on n-butanol proximity of ≤5.0 Å from the extractant.

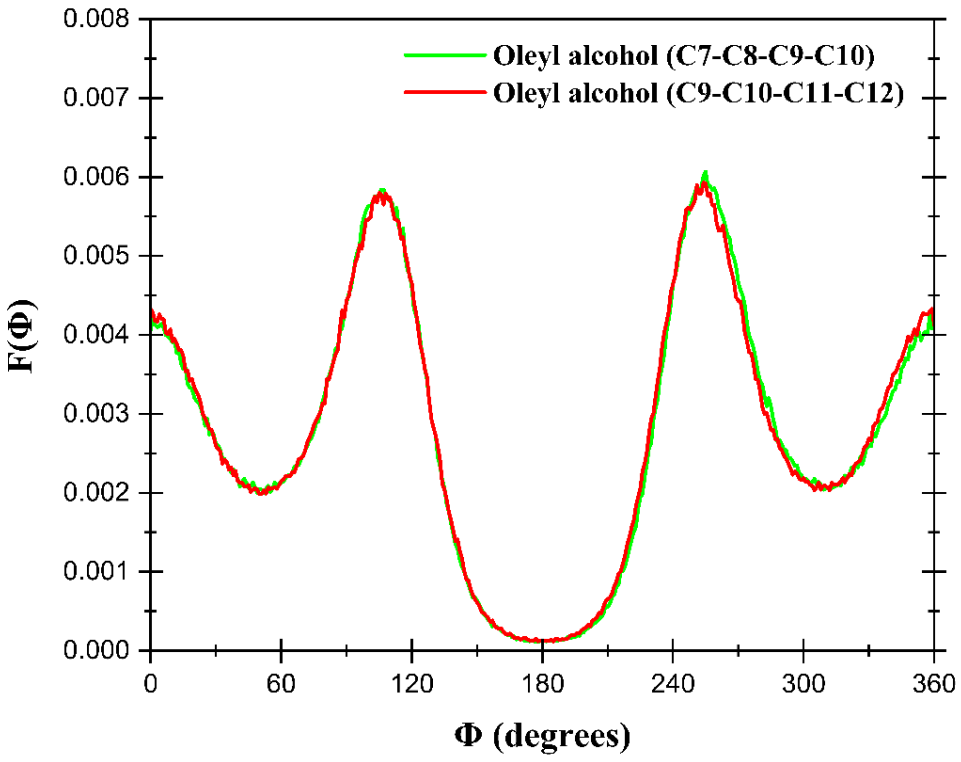
The capture of n-butanol was found to be dependent on the molecular structure of the extractant molecules. At the lowest simulated concentration of 50 ml/l, all five extractants demonstrated capture efficiencies of more than 80%. Extractants such as oleyl alcohol and 2-ethyl-1-hexanol were found facilitate more absorption of n-butanol compared to other solvents. Solvents such as benzyl benzoate captured least amount of n-butanol that can be attributed to the presence of two rigid aromatic groups that inhibits the flexibility

for capture and sterically prevents interaction with butanol to some extent compared to others. Further rise in the extractant concentration from 50 to 100 ml/l showed almost 7.4-9.7% rise in the n-butanol capture, resulted in almost the same trend demonstrating highest efficiencies for branched 2-ethyl-1-hexanol and bent oleyl alcohol structures.

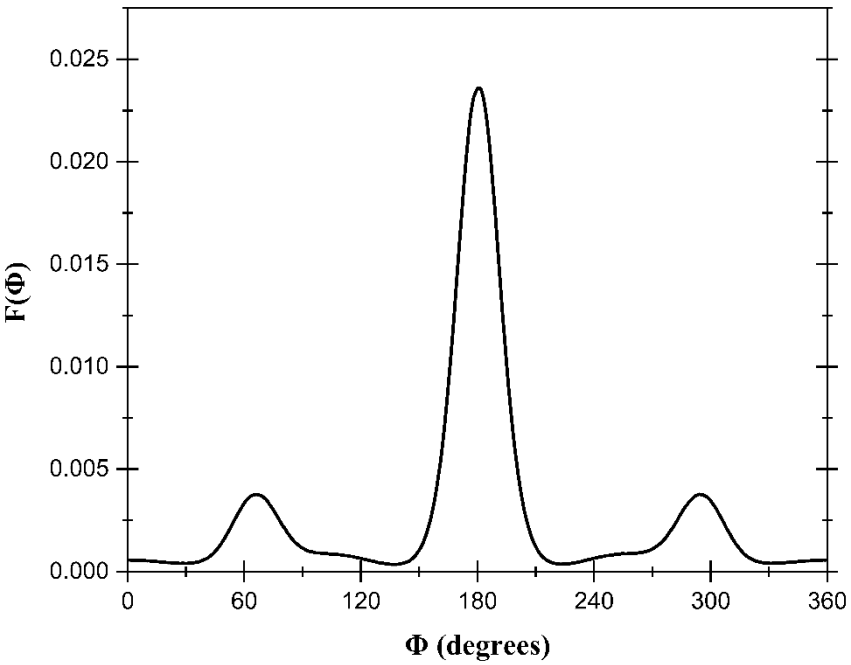
With further rise in the extractant concentration from 100 to 250 ml/l, resulted in capture efficiencies being crossed above 90% by all five extractants (Figure 4.1). The simulation results again indicated higher absorption of butanol by structures such as oleyl alcohol and 2-ethyl-1-hexanol and considerably lower for structurally rigid or linear molecules such as benzyl benzoate and n-decanol respectively. Oleyl alcohol was found to demonstrate highest efficiency of 98.42% among all the extractants for all the simulated concentrations. The dominant nature of oleyl alcohol for absorbing n-butanol with higher selectivity values has been earlier proved by liquid-liquid extraction experimental studies as well as computational thermodynamic models such as NRTL, UNIQUAC and COSMO-SAC[29,63,64]. This higher uptake of n-butanol by oleyl alcohol is primarily due to the reorganization of its long and flexible hydrophobic chain into bent structure in aqueous media, due to the presence of a double bond between its 9th and 10th carbon atoms, capable of encapsulating multiple butanol molecules inside.

4.2 Structural Influence on Capture: Dihedral Angle Analysis

(a)



(b)



(c)

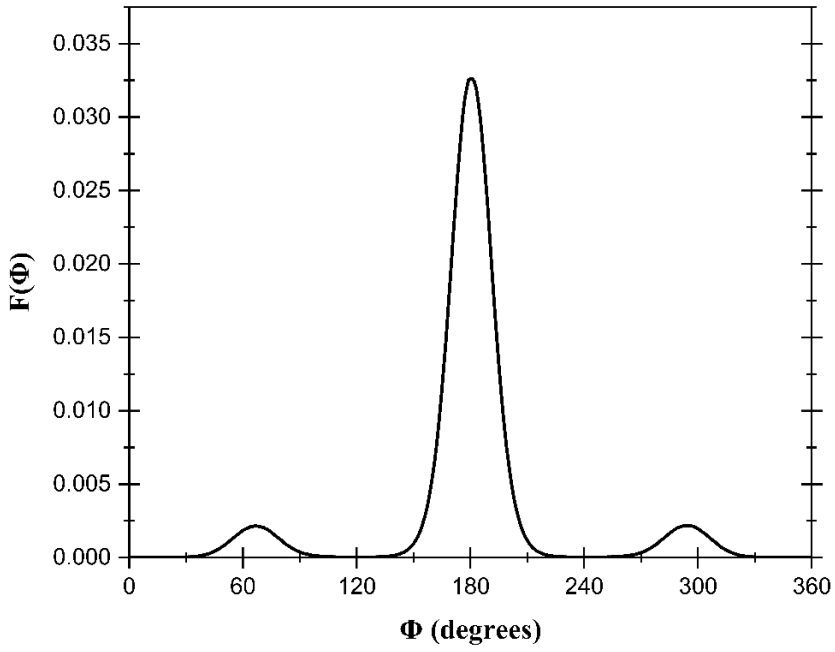


Fig. 4.2. Dihedral angle distributions of (a) C7-C8-C9-C10 and C9-C10-C11-C12 dihedral angles of oleyl alcohol that contains a double bond at C9-C10, (b) complete oleyl alcohol carbon backbone and (c) complete n-decanol carbon backbone.

The bent structure of oleyl alcohol in simulated system can be explained by evaluating dihedral angle distributions for the C7-C8-C9-C10 and C9-C10-C11-C12 dihedral angles (Figure 4.2a). The dihedral angle distribution of these two dihedrals incorporating the double bond from both sides demonstrated that the oleyl alcohol majorly adopts non-trans configuration, indicating the twists within its structure. The lowest capture efficiency was demonstrated by n-decanol that possesses almost straight conformation that doesn't bend easily. The straight structure of n-decanol can be also proved by its more trans-dominated dihedral angle distribution calculated for the carbon backbone of the chain (Figure 4.2c), compared to that of the oleyl alcohol (Figure 4.2b). Decanol therefore finds it difficult to adapt and wrap around the n-butanol molecules more readily as of oleyl alcohol, always resulting in lower capture efficiencies. These limitations restrict its ability to efficiently separate n-butanol specially at the higher concentrations. This behaviour is similar to increasing the chain length in diglycolamide extractants that makes them less effective, as they can't move freely and change the shape easily to capture more molecules within their domains[65]. Upon further rise in the extractant concentration from 250 to 300 ml/l, we found decreasing trend of extraction efficiencies for almost all the extractants, except 2-ethyl-1-hexanol, that still showed lesser efficiency compared to oleyl alcohol. The excellent capacity of oleyl alcohol to capture n-butanol from water is visualized by VMD (Figure 4.3).

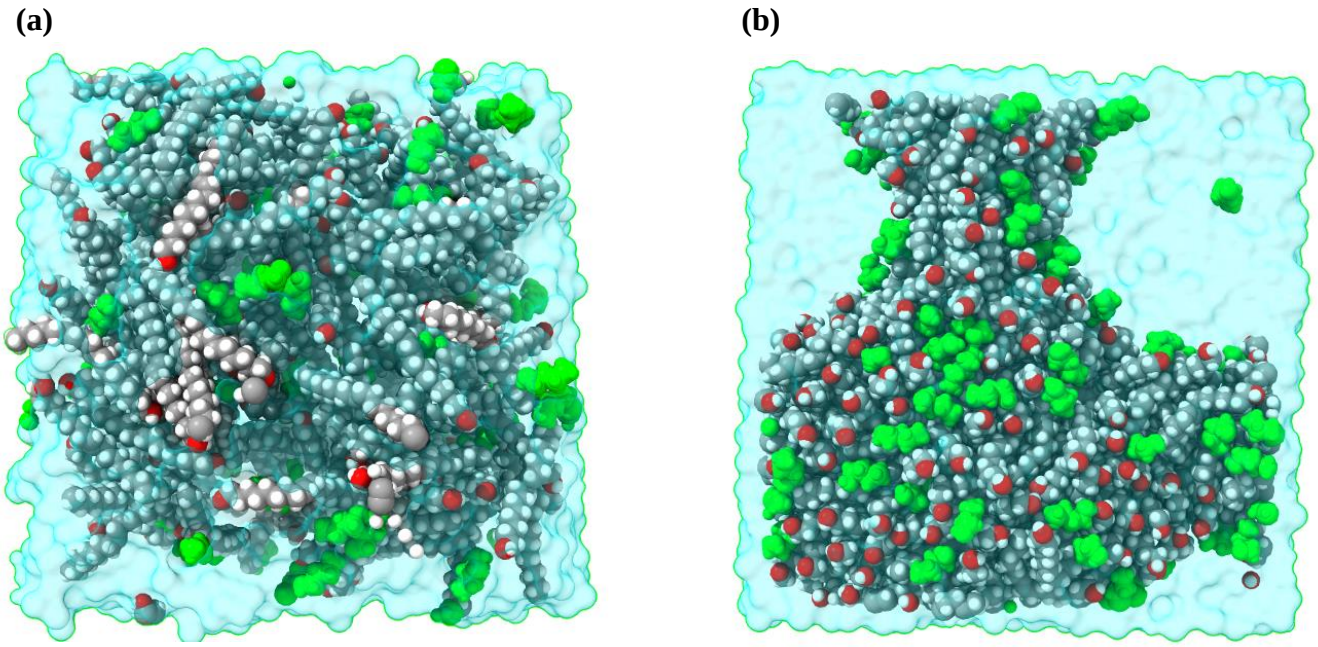


Fig. 4.3. Simulation snapshots showing (a) initial and (b) final configurations of molecular dynamics simulation of butanol-extractant-water system demonstrating selective capture of n-butanol (green) within aggregated oleyl alcohol (grey) in aqueous solution (blue) for 300 ml/l oleyl alcohol and 30 g/l n-butanol system.

4.3 Effect of Butanol Concentration on Extraction Efficiency

The next set of simulations were carried out to understand the impact of variation of n-butanol concentration on the capturing efficiencies. Five different simulations with varying n-butanol concentration of 10 to 50 g/l were carried out by utilizing each extractant with a concentration of 100 ml/l (Figure 4.4). 4-n-

butylphenol demonstrated highest susceptibility to change in butanol capture by around 9.3% from 10 to 50 g/l butanol concentration. Rigid structures such as benzyl benzoate do not offer much variation in n-butanol capture with increasing n-butanol concentration. While 4-n-butylphenol and 2-ethyl-1-hexanol showed increasing trend in the capture efficiencies, oleyl alcohol and n-decanol showed decreasing trend. This indicates that with increasing n-butanol concentration, the small size solvents such as 4-n-butylphenol and 2-ethyl-1-hexanol favours more n-butanol penetration within their aggregated moieties, whereas within long-size structures such as oleyl alcohol and decanol, n-butanol struggles to find space possibly due to the geometric hindrance caused by overlapping chains that leaves comparatively less space for interior capture. Further, a single oleyl alcohol and decanol molecule, both has only one -OH group to interact with n-butanol with hydrogen bonding. Upon increasing the n-butanol concentration, but still keeping the extractant concentration same, leads to limited offering of -OH groups for hydrogen bonding, results into the saturation of n-butanol capture (Figure 4.4). Oleyl alcohol, still, due to its slightly bent structure always captures more amount of n-butanol compared to n-decanol. This concludes that the utilization of highly effective oleyl alcohol should be done for lower concentrations of n-butanol that are normally found in the fermentation broths.

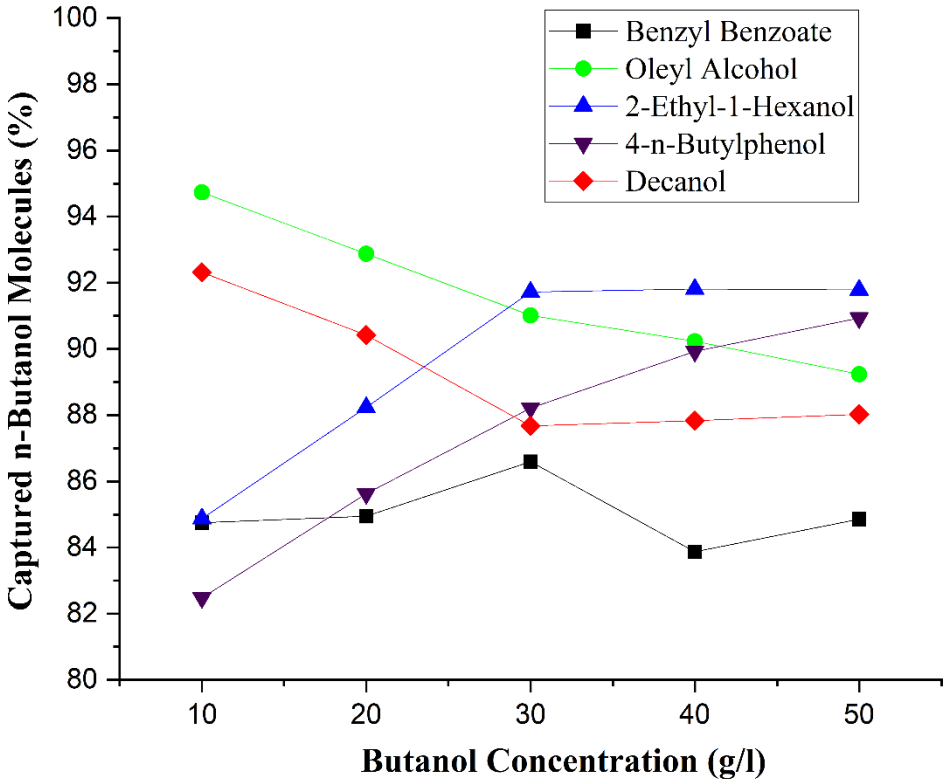


Fig. 4.4. The effect of variation of butanol concentration (10–50 g/L) on the capture efficiency of five organic extractants with 100 ml/l concentration.

4.4 Hydrogen Bonding Analysis

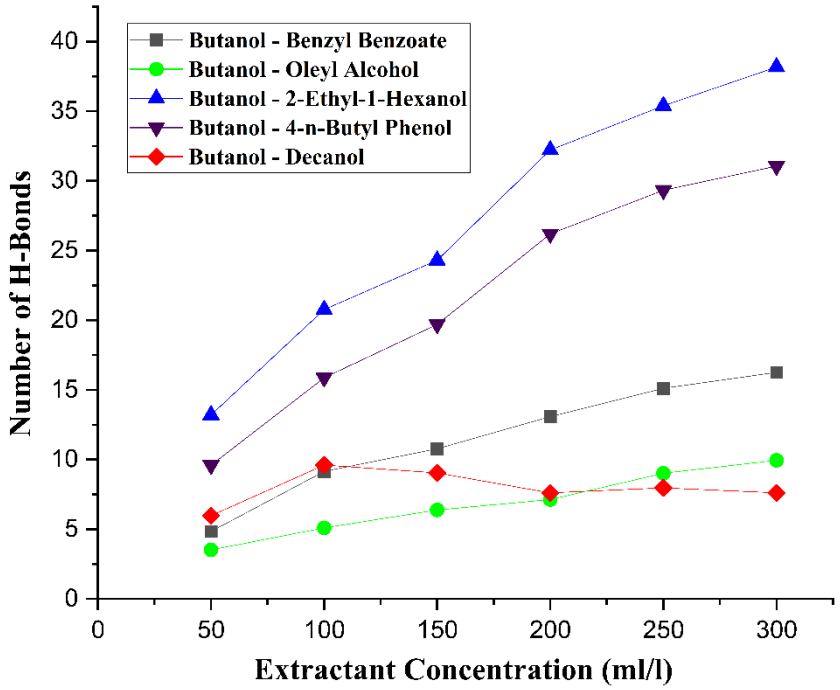
The next set of calculations are carried out to understand the effect of hydrogen bonding between (i) butanol-extractant, (ii) extractant-water and (iii) butanol-water to check its effect on n-butanol capture (Figure 4.5a-4.5c). Theoretically, a single molecule of n-butanol can form two hydrogen bonds with oleyl alcohol, 2-ethyl-1-hexanol, 4-n-butylphenol and n-decanol, whereas with benzyl benzoate only a single hydrogen bond could be formed.

Following this criterion and observing the number of hydrogen bonds between extractant and n-butanol, it can be found that benzyl benzoate forms a smaller number of hydrogen bonds compared to 2-ethyl-1-hexanol and 4-n-butylphenol (Figure 4.5a). However, again, due to the long chain structures and presence of a single -OH group at the extreme end of the chains of both oleyl alcohol and n-decanol, a smaller number of hydrogen bonds formation could be observed compared to benzyl benzoate. Although, hydrogen bonding is not the only criteria for n-butanol capture. The interaction of the other parts of the extractants such as the hydrophobic tail and aromatic groups with n-butanol decides the total n-butanol capture. Also, the interaction between extractant-water and butanol-water decides the overall fate of the final capture efficiency.

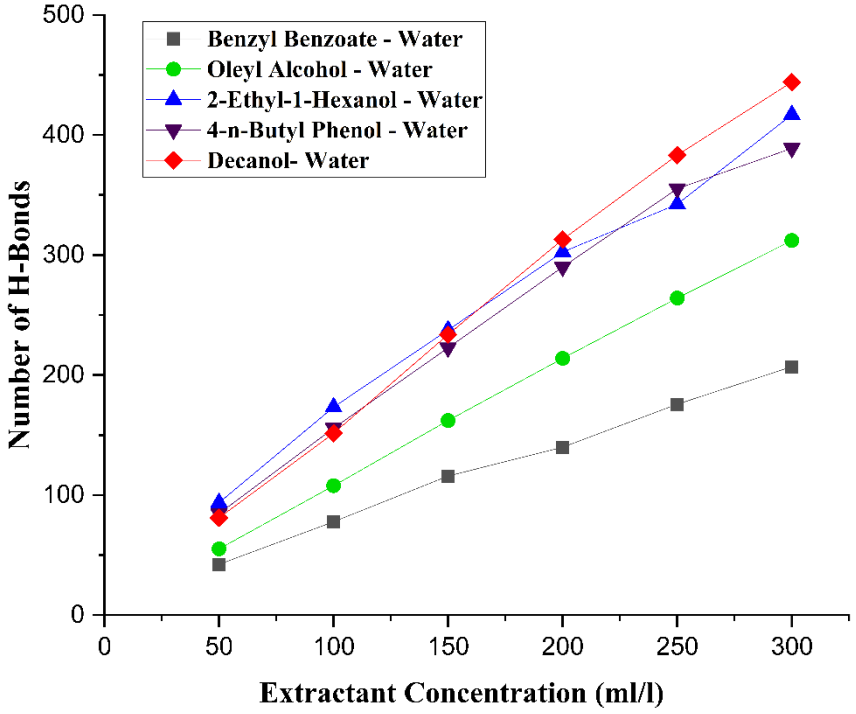
It could be observed that the extractant which forms a smaller number of hydrogen bonds with water in the presence of n-butanol can be more efficient for n-butanol capture (Figure 4.5b). Benzyl benzoate due to its limited hydrogen bonding capacity and nonpolar aromatic structure, as discussed earlier, demonstrates least number of hydrogen bonds with polar water too.

Oleyl alcohol, which is having similar hydrogen bonding capacity with water compared to 2-ethyl-1-hexanol, 4-n-butylphenol and n-decanol, still shows least number of extractant-water hydrogen bonds. This characteristic is supportive for n-butanol extraction, since it implies an affinity for clustering around hydrophobic species rather than interacting with water, which as a consequence can be related to its higher butanol capture capacity compared to the three solvents. The number of extractant-water hydrogen bonds are further observed to illustrate a systematic rise with increasing the extractant concentration from 50 to 300 ml/l for all five solvents (Figure 4.5b).

(a)


Butanol - Benzyl Benzoate
Butanol - Oleyl Alcohol
Butanol - 2-Ethyl-1-Hexanol
Butanol - 4-n-Butyl Phenol
Butanol - Decanol
Number of H-Bonds
Extractant Concentration (ml/l)
0
5
10
15
20
25
30
35
40
0
50
100
150
200
250
300

(b)


Benzyl Benzoate - Water
Oleyl Alcohol - Water
2-Ethyl-1-Hexanol - Water
4-n-Butyl Phenol - Water
Decanol- Water
Number of H-Bonds
Extractant Concentration (ml/l)
0
100
200
300
400
500
0
50
100
150
200
250
300

(c)

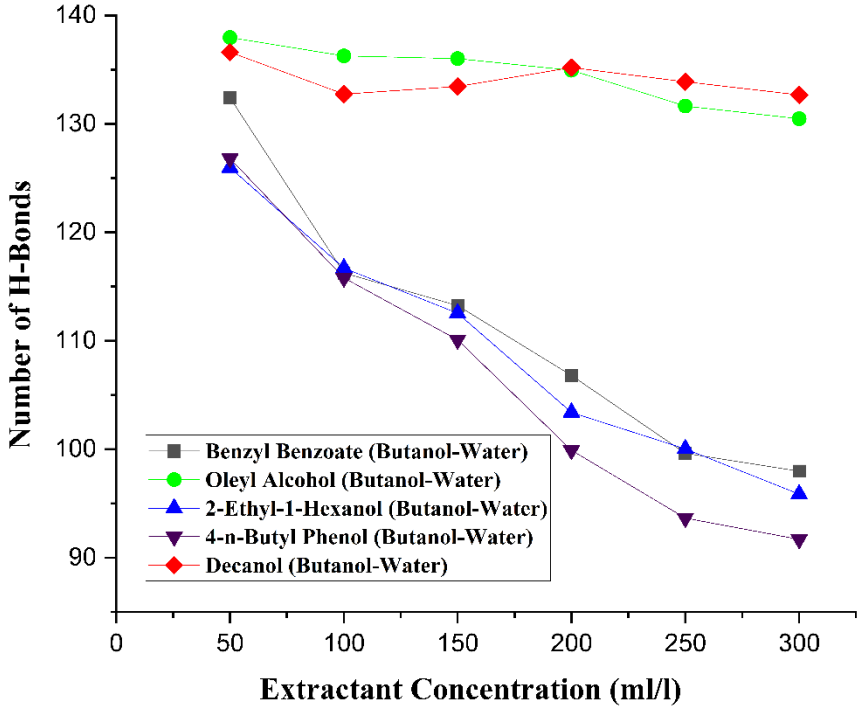


Fig. 4.5. The number of hydrogen bonds between (a) butanol-extractant, (b) extractant-water and (c) butanol-water as a function of extractant concentration.

The hydrogen bonding between n-butanol and water in the presence of extractant also shows a somewhat opposite trend to butanol-extractant hydrogen bonding (Figure 4.5c and 4.5a). Both n-decanol as well as oleyl alcohol, due to their long chains and availability of large number of hydrogen atoms for bonding with water oxygen atoms demonstrates significantly high number of hydrogen bonds. This can be directly connected with the least capacity of n-decanol for n-butanol capture observed earlier (Figure 4.1). Despite a similar nature of higher butanol-water hydrogen bonding, oleyl alcohol, on the other hand, shows excellent n-butanol capture due to its extremely lesser number of hydrogen bonding with water (less than ~100 hydrogen bonds for higher extractant concentrations) compared to n-decanol (Figure 4.5b). Other three extractants demonstrate quite low number of butanol-water hydrogen bonds compared to n-decanol and oleyl alcohol and show continuous decrease in hydrogen bonding with increasing concentrations of extractants. The comparison of hydrogen bonding between butanol-extractant, extractant-water and butanol-water indicates that the extractant-water interactions has most dominating effect except for benzyl benzoate, whereas the butanol-extractant and butanol-water interactions have the stabilizing effect on the overall n-butanol capture.

Table 4.1 Hydrogen Bond Interactions Among Extractant, *n*-Butanol, and Water at Varying Extractant Concentrations for Five Organic Solvent Systems.

Table 4.1 (a)

The number of hydrogen bonds between extractant-butanol, water-butanol, extractant-water in the benzyl benzoate extractant system.

extractant concentration (ml/l)	extractant-butanol	butanol-water	water-extractant
50	4.85	132	42.28
100	9.15	116.25	77.88
150	10.77	113.25	115.88
200	13.08	106.80	139.87
250	15.11	99.63	175.68
300	16.25	97.98	207.02

Table 4.1 (b)

The number of hydrogen bonds between extractant-butanol, water-butanol, extractant-water in the oleyl alcohol extractant system.

extractant concentration (ml/l)	extractant-butanol	butanol-water	water-extractant
50	3.52	137.96	55.11
100	5.10	136.25	107.84
150	5.83	136.01	162.08
200	7.13	134.93	213.93
250	9.01	131.63	264.21
300	9.94	130.48	312.12

Table 4.1 (c)

The number of hydrogen bonds between extractant-butanol, water-butanol, extractant-water in the 2-ethyl-1-hexanol extractant system.

extractant concentration (ml/l)	extractant-butanol	butanol-water	water-extractant
50	13.20	125.96	93.61
100	20.76	116.70	173.38
150	24.30	112.53	237.52
200	32.22	103.39	302.55
250	35.38	100.03	342.45
300	38.17	95.85	416.90

Table 4.1 (d)

The number of hydrogen bonds between extractant-butanol, water-butanol, extractant-water in the 4-n-butyl phenol extractant system.

extractant concentration (ml/l)	extractant-butanol	butanol-water	water-extractant
50	9.59	126.80	84.62
100	15.87	115.80	155.81
150	19.69	110.08	222.63
200	26.19	99.90	290.00
250	29.33	93.65	355.25
300	31.06	91.68	388.94

Table 4.1 (e)

The number of hydrogen bonds between extractant-butanol, water-butanol, extractant-water in the n-decanol extractant system.

extractant concentration (ml/l)	extractant-butanol	butanol-water	water-extractant
50	5.97	136.60	81.08
100	9.61	132.75	151.48
150	9.04	133.44	233.77
200	7.61	135.19	312.92
250	7.97	133.88	383.33
300	7.61	132.67	444.06

4.5 Effect of Temperature on Butanol Capture.

The final set of simulations were carried out to understand the effect of temperature variation on the n-butanol capture by extractants. Oleyl alcohol, the extractant which demonstrated the highest capture efficiencies in the earlier studies was chosen to conduct temperature studies at 275 K, 300 K and 325 K. Two set of simulations were carried out by choosing the extractant concentration of 50 ml/l consisting of 30 oleyl alcohol and 300 ml/l consisting of 177 oleyl alcohol molecules. The capture efficiencies were found to increase by decreasing temperature and vice versa for both the simulated concentrations. In case of 50 ml/l concentration, the efficiency decreased from 83.83% at 300 K to 82.64% at 325 K, whereas it increased to 87.25% at 275 K. For 300 ml/l extractant concentration, the efficiency reduced from 97.05% at 300 K to 95.61% at 325 K and augmented to 98.37% at 275 K. It is apparent that with the rise in temperature, the attractive interactions such as between oleyl alcohol and n-butanol reduces, hence, higher n-butanol capture for the commercial purposes can be achieved at lower temperatures.

5. Conclusions

The molecular dynamics simulations of n-butanol extraction from the aqueous solution using five organic solvents, namely, benzyl benzoate, oleyl alcohol, 2-ethyl-1-hexanol, 4-nbutylphenol, and n-decanol have been carried out for various concentrations of extractants and n-butanol. Oleyl alcohol was found to demonstrate highest n-butanol capturing efficiency of 98.42% among all the five solvents at 300K temperature and 1 bar pressure conditions and 250 ml/l extractant concentration and 30 g/l n-butanol concentration. The higher n-butanol uptake by oleyl alcohol is attributed to its long chain and specifically the bent structure near its almost centrally located double bond, that has been concluded based on the dihedral angle distributions of its C7-C8-C9-C10 and C9-C10-C11-C12 dihedrals. Both of these dihedral angles were found to adopt high-energy sterically unusual non-trans dihedral conformations that results into a somewhat bent structure capable of capture more amount of n-butanol within its curved space. Contrary to this observation, n-decanol, which also possesses a long-chain structure demonstrates lowest n-butanol capture capacity, especially at higher extraction concentrations, due to its highly trans-dominated carbon backbone depicted using the dihedral angle distribution. Other solvents such as benzyl benzoate also captured less amount of n-butanol due to the absence of flexibility within the structure due to the rigid aromatic groups that sterically avoids higher interaction with butanol. 2-ethyl-1-hexanol, on the other hand, demonstrated slightly less n-butanol capture than oleyl alcohol, but considerably higher than benzyl benzoate and n-decanol due to its branched structure capable of capturing more n-butanol within its branches.

The variation of n-butanol concentration from 10-50 g/l with fixed extractant concentration at 100 ml/l again showed highest n-butanol uptake among all five extractants especially at n-butanol concentrations of $\leq$ 30 g/l, suitable for extraction of n-butanol from the fermentation broths. 4-n-butylphenol demonstrates highest variation in n-butanol capture by around 9.3%, whereas rigid structures such as benzyl benzoate do not offer much variation in the capture percentage with change in n-butanol concentration from 10 to 50 g/l. The analysis of hydrogen bonding between butanol-extractant, extractant-water and butanol-water for all five extractants indicates that the extractant-water interactions have the dominating effect for most of the solvents except benzyl benzoate that correlates with the overall n-butanol capture. The effect of temperature variation carried out for the most effective oleyl alcohol extractant from 275 to 325 K for two diverse extractant concentrations concludes higher uptake of n-butanol at lower temperatures. The overall n-butanol extraction efficiency, hence, is found to be controlled by multiple factors such as the shape and size of the extractants, hydrogen bonding especially between extractant-water as well as butanol-extractant and butanol-water, concentrations of n-butanol and extractants, and the temperature.

6. Annexure

Annexure I: Simulation Input Files and Scripts.

I.1 Custom Python Analysis Scripts and the Packmol script

- **I.1.1: - Capture Efficiency Calculation Script**

```
import MDAnalysis as mda
from MDAnalysis.analysis.distances import distance_array
import numpy as np

# Load GROMACS topology and trajectory files
u = mda.Universe("prd2.gro", "prd2.xtc")

# Select all atoms for n-butanol and Decanol
butanol_atoms = u.select_atoms("resname BUT")  # All atoms in n-butanol
decanol_atoms = u.select_atoms("resname BPH")  # All atoms in Decanol

# Define distance threshold for capture (in Angstroms)
threshold = 5.0

# Total number of atoms in the simulation
total_atoms = len(u.atoms)

# Store results
captured_counts = []
output_file = "1captured_molecules_with_atom_count.txt"

# Open output file for writing results
with open(output_file, "w") as f:
```

```
    f.write("Frame\tCaptured_Molecules\tTotal_Atoms\n")

    # Iterate through each frame of the trajectory
    for ts in u.trajectory:
        # Initialize a set to store captured molecule IDs for n-butanol
        captured_molecules = set()

        # Loop through all residues of n-butanol
        for res_but in butanol_atoms.residues:
            # Get positions of all atoms in this n-butanol molecule
            butanol_positions = res_but.atoms.positions

            # Calculate distances to all decanol atoms
            distances = distance_array(butanol_positions, decanol_atoms.positions, box=u.dimensions)

            # Check if any atom in this molecule is within the threshold distance
            if np.any(distances <= threshold):
                captured_molecules.add(res_but.resid)  # Add the molecule ID (resid) to the captured set

        # Store the number of captured molecules for this frame
        captured_counts.append(len(captured_molecules))
       # Write results for this frame to the output file
        f.write(f"{ts.frame}\t{len(captured_molecules)}\t{total_atoms}\n")

# Calculate the average number of captured molecules
average_captured = np.mean(captured_counts)
```

```
# Write the average captured number and total atoms to the output file
with open(output_file, "a") as f:
    f.write(f"\nAverage Captured Molecules: {average_captured:.2f}\n")
    f.write(f"Total Atoms in Simulation: {total_atoms}\n")

# Print the average number of captured molecules to the screen
print(f"Average Number of Captured Molecules: {average_captured:.2f}")
```

- **I.1.2: - Hydrogen Bond Analysis Script.**

```
#!/bin/bash
# Load GROMACS environment
source /usr/local/gromacs/bin/GMXRC
# Define file names
GRO="prd2.gro"
TPR="prd2.tpr"
XTC="prd2.xtc"
NDX="index.ndx"

# Create index file
gmx_mpi make_ndx -f $GRO -o $NDX <<EOF
q
EOF

# Run hydrogen bond analysis
gmx_mpi hbond -f $XTC -s $TPR -n $NDX -num water_but.xvg <<EOF
4
2
EOF
```

```
gmx_mpi hbond -f $XTC -s $TPR -n $NDX -num water_solvent.xvg <<EOF
4
3
EOF

gmx_mpi hbond -f $XTC -s $TPR -n $NDX -num butanol_solvent.xvg <<EOF
2
3
EOF

# Extract averages
AVG_WATER_BUT=$(awk '{sum+=$2} END {print sum/NR}' water_but.xvg)
AVG_WATER_SOLVENT=$(awk '{sum+=$2} END {print sum/NR}' water_solvent.xvg)
AVG_BUTANOL_SOLVENT=$(awk '{sum+=$2} END {print sum/NR}' butanol_solvent.xvg)

# Print results
echo "Average Hydrogen Bonds:"
echo "Water - Butanol: $AVG_WATER_BUT"
echo "Water - Solvent: $AVG_WATER_SOLVENT"
echo "Butanol - Solvent: $AVG_BUTANOL_SOLVENT"
```

- **I.1.3: - Dihedral Angle Distribution Script for index file generation.**

```
#!/usr/bin/env python3
"""
generate_oleyl_dihedrals_ndx.py

Scan a GROMACS .gro file for oleyl alcohol residues (resname OLE),
```

```
extract carbon atom indices (excluding OH), and generate a single
ndx group listing all consecutive dihedrals along the alkyl chain.

Usage:
    python generate_oleyl_dihedrals_ndx.py input.gro [output.ndx]

If output name is omitted, uses `<input_basename>_dihedrals.ndx`.
Produces:
  [ BASENAME_DIHEDRALS ]
    idx1  idx2  idx3  idx4
    ...
Without serial numbers.
"""
import sys
import os
import re

def generate_dihedral_ndx(gro_filename, output_ndx_filename):
    # Read GRO file lines
    with open(gro_filename, 'r') as f:
        lines = f.readlines()
    atom_lines = lines[2:-1]  # skip header and box

    # Map residue ID to atoms
    oleyl_residues = {}
    for line in atom_lines:
        try:
```

```
        res_id = int(line[0:5])
        atom_idx = int(line[15:20])
    except ValueError:
        continue
    res_name = line[5:10].strip()
    atom_name = line[10:15].strip()
    if res_name == 'OLE':
        oleyl_residues.setdefault(res_id, {})[atom_name] = atom_idx

# Identify carbon atoms
carbon_rx = re.compile(r'^C(\d+)$')
dihedrals = []
# For each residue, order carbons and form dihedrals
for atoms in sorted(oleyl_residues.values(), key=lambda d: min(d.values())):
    carbons = [(int(m.group(1)), idx)
               for name, idx in atoms.items()
               if (m := carbon_rx.match(name))]
    carbons.sort(key=lambda x: x[0])
    for i in range(len(carbons) - 3):
        group = [carbons[i+j][1] for j in range(4)]
        dihedrals.append(group)

# Derive group name from input GRO basename
base = os.path.splitext(os.path.basename(gro_filename))[0].upper()
group_name = base + '_DIHEDRALS'

# Write index file
```

```
    with open(output_ndx_filename, 'w') as out:
        out.write(f"[ {group_name} ]\n")
        for grp in dihedrals:
            out.write("  " + "  ".join(str(x) for x in grp) + "\n")

    print(f"Wrote {len(dihedrals)} dihedrals to '{output_ndx_filename}'")

if __name__ == '__main__':
    if len(sys.argv) not in (2, 3):
        print(f"Usage: {os.path.basename(sys.argv[0])} input.gro [output.ndx]")
        sys.exit(1)
    inp = sys.argv[1]
    if not os.path.isfile(inp):
        print(f"Error: '{inp}' not found.")
        sys.exit(1)
    out = sys.argv[2] if len(sys.argv) == 3 else os.path.splitext(inp)[0] + '_dihedrals.ndx'
    generate_dihedral_ndx(inp, out)
```

- **I.1.4: - Dihedral Angle Distribution Script for plotting.**

```
#!/usr/bin/env python3
"""
dihedral_convert_and_plot.py

Reads GROMACS .xvg dihedral distribution files (angles -180..180),
converts angles to a 0–360° scale in memory, saves the processed data
as CSV for Excel import, then plots and saves each distribution
as a PNG image, finally displaying the plot on screen.
```

```
Removes the bottom axis spine (x-axis line).


Usage:
    python dihedral_convert_and_plot.py file1.xvg file2.xvg ...
    python dihedral_convert_and_plot.py       # processes all *.xvg in CWD
"""
import sys
import glob
import os
import numpy as np
import matplotlib.pyplot as plt



def load_and_convert(path):
    """
    Load a .xvg file and convert its first-column angles from -180..180 to 0..360:
      0..180   → unchanged
      -180..-1→ +361  (so -180→181, -1→360)
      angle >= 0 → angle
      angle < 0  → angle + 361  (so -180→181, -1→360)
    Returns angles and values arrays.
    """
    raw = np.loadtxt(path, comments=('#', '@'))
    angles, vals = raw[:,0], raw[:,1]
    angles_conv = np.where(angles >= 0, angles, angles + 361.0)
    return angles_conv, vals
```

```
def save_for_excel(angles, vals, infile):
    """
    Save processed angles and values to CSV for Excel.
    """
    basename = os.path.splitext(os.path.basename(infile))[0]
    csv_name = f"{basename}_0to360.csv"
----------------------py
    data = np.column_stack((angles, vals))
    header = 'Angle,Probability'
    np.savetxt(csv_name, data, delimiter=',', header=header, comments='')
    print(f"Saved Excel data to {csv_name}")



def plot_and_save(angles, vals, infile):
    """
    Plot the distribution, hide the bottom spine, and save as PNG.
    """
    basename = os.path.splitext(os.path.basename(infile))[0]
    fig, ax = plt.subplots()
    ax.plot(angles, vals, linewidth=2)
    ax.set_xlabel('Dihedral Angle (°)')
    ax.set_ylabel('Probability')
    ax.set_title(basename)
    # Hide bottom axis line
    ax.spines['bottom'].set_visible(False)
    # Keep x-ticks without the spine line
```

```
    ax.xaxis.set_ticks_position('none')


    plt.tight_layout()
    png_name = f"{basename}_0to360.png"
    plt.savefig(png_name)
    print(f"Saved plot to {png_name}")
    plt.show()



def main():
    # Determine input .xvg files
    inputs = sys.argv[1:] if len(sys.argv) > 1 else glob.glob('*.xvg')
    if not inputs:
        print("No .xvg files found to process.")
        return

    for infile in sorted(inputs):
        if not os.path.isfile(infile):
            print(f"Warning: '{infile}' not found, skipping.")
            continue
        angles, vals = load_and_convert(infile)
        save_for_excel(angles, vals, infile)
        plot_and_save(angles, vals, infile)

if __name__ == '__main__':
    main()
```

I.2 Parameterized Molecule Files (.mol2)

- **I.2.1 n-Butanol (n-butanol.mol2)**

GAFF-parameterized file with AM1-BCC partial charges.

<TRIPOS>MOLECULE

BUT

15 14 1 0 0

SMALL

bcc

@<TRIPOS>ATOM

1 C -0.0520 -0.0080 0.0130 c3 1 BUT -0.092100

2 C1 1.4790 -0.0010 0.0040 c3 1 BUT -0.079400

3 C2 2.0570 0.7100 -1.2250 c3 1 BUT -0.084400

4 C3 3.5740 0.7170 -1.2410 c3 1 BUT 0.131400

5 O 3.9870 1.4080 -2.4290 oh 1 BUT -0.601800

6 H -0.4460 1.0020 0.0110 hc 1 BUT 0.034367

7 H1 -0.4370 -0.5130 0.8910 hc 1 BUT 0.034367

8 H2 -0.4430 -0.5180 -0.8620 hc 1 BUT 0.034367

9 H3 1.8440 -1.0250 0.0370 hc 1 BUT 0.037700

10 H4 1.8410 0.4830 0.9080 hc 1 BUT 0.037700

11 H5 1.7090 1.7370 -1.2600 hc 1 BUT 0.055700

12 H6 1.7070 0.2300 -2.1330 hc 1 BUT 0.055700

13 H7 3.9590 -0.2980 -1.2440 h1 1 BUT 0.019700

14 H8 3.9610 1.2210 -0.3610 h1 1 BUT 0.019700

15 H9 4.9310 1.4650 -2.5290 ho 1 BUT 0.398000

@<TRIPOS>BOND

1 1 2 1

2 1 6 1

```
     3    1    7 1
     4    1    8 1
     5    2    3 1
     6    2    9 1
     7    2   10 1
     8    3    4 1
     9    3   11 1
    10    3   12 1
    11    4    5 1
    12    4   13 1
    13    4   14 1
    14    5   15 1
@<TRIPOS>SUBSTRUCTURE
     1 BUT         1 TEMP              0 ****  ****    0 ROOT
```

- **I.2.2 n-Decanol (n-decanol.mol2)**

  Long-chain alcohol molecule used as extractant, parameterized using antechamber.

```
@<TRIPOS>MOLECULE
BUT
  33   32    1    0    0
SMALL
bcc
@<TRIPOS>ATOM
      1 C          -0.2010    -0.0680     0.1040 c3        1 BUT      -0.092100
      2 C1          1.3290    -0.0380     0.0820 c3        1 BUT      -0.080400
      3 C2          1.8960     0.6660    -1.1570 c3        1 BUT      -0.079400
      4 C3          3.4280     0.6930    -1.1900 c3        1 BUT      -0.079400
```

5	C4	3.9930	1.4040	-2.4250	c3	1 BUT -0.079400
6	C5	5.5250	1.4250	-2.4620	c3	1 BUT -0.079400
7	C6	6.0900	2.1420	-3.6930	c3	1 BUT -0.078400
8	C7	7.6220	2.1560	-3.7340	c3	1 BUT -0.078400
9	C8	8.1780	2.8810	-4.9630	c3	1 BUT -0.084400
10	C9	9.6940	2.8900	-5.0040	c3	1 BUT 0.131400
11	O	10.0890	3.5940	-6.1910	oh	1 BUT -0.601800
12	H	11.0300	3.6530	-6.3060	ho	1 BUT 0.398000
13	H1	-0.6110	0.9370	0.0930	hc	1 BUT 0.032700
14	H2	-0.5730	-0.5670	0.9930	hc	1 BUT 0.032700
15	H3	-0.5940	-0.5940	-0.7600	hc	1 BUT 0.032700
16	H4	1.7110	-1.0550	0.1220	hc	1 BUT 0.038700
17	H5	1.6940	0.4620	0.9760	hc	1 BUT 0.038700
18	H6	1.5160	1.6850	-1.1940	hc	1 BUT 0.039700
19	H7	1.5260	0.1690	-2.0510	hc	1 BUT 0.039700
20	H8	3.8060	-0.3260	-1.1580	hc	1 BUT 0.038700
21	H9	3.7970	1.1850	-0.2920	hc	1 BUT 0.038700
22	H10	3.6190	2.4260	-2.4540	hc	1 BUT 0.039700
23	H11	3.6190	0.9160	-3.3230	hc	1 BUT 0.039700
24	H12	5.8990	0.4030	-2.4390	hc	1 BUT 0.039700
25	H13	5.9000	1.9080	-1.5620	hc	1 BUT 0.039700
26	H14	5.7220	3.1660	-3.7130	hc	1 BUT 0.041700
27	H15	5.7130	1.6630	-4.5940	hc	1 BUT 0.041700
28	H16	7.9880	1.1320	-3.7180	hc	1 BUT 0.039700
29	H17	7.9980	2.6310	-2.8290	hc	1 BUT 0.039700
30	H18	7.8300	3.9090	-4.9820	hc	1 BUT 0.055700
31	H19	7.8150	2.4120	-5.8720	hc	1 BUT 0.055700

32 H20 10.0800 1.8750 -5.0260 h1 1 BUT 0.019700

33 H21 10.0960 3.3840 -4.1250 h1 1 BUT 0.019700

@<TRIPOS>BOND

1 1 2 1

2 1 13 1

3 1 14 1

4 1 15 1

5 2 3 1

6 2 16 1

7 2 17 1

8 3 4 1

9 3 18 1

10 3 19 1

11 4 5 1

12 4 20 1

13 4 21 1

14 5 6 1

15 5 22 1

16 5 23 1

17 6 7 1

18 6 24 1

19 6 25 1

20 7 8 1

21 7 26 1

22 7 27 1

23 8 9 1

24 8 28 1

25 8 29 1

26 9 10 1

27 9 30 1

28 9 31 1

29 10 11 1

30 10 32 1

31 10 33 1

32 11 12 1

@<TRIPOS>SUBSTRUCTURE

1 BUT 1 TEMP 0 **** **** 0 ROOT

- **I.2.3 Benzyl Benzoate (benzyl_benzoate.mol2)**

Aromatic ester extractant with bulky molecular structure.

@<TRIPOS>MOLECULE

BEN

28 29 1 0 0

SMALL

bcc

@<TRIPOS>ATOM

1 C 0.1220 -0.0600 0.0010 ca 1 BEN -0.071000

2 C1 1.4980 0.0940 0.0010 ca 1 BEN -0.147000

3 C2 -0.7050 1.0600 0.0000 ca 1 BEN -0.135600

4 C3 2.0510 1.3670 -0.0010 ca 1 BEN -0.096000

5 C4 -0.1480 2.3340 -0.0010 ca 1 BEN -0.071000

6 C5 1.2290 2.4860 -0.0020 ca 1 BEN -0.147000

7 C6 -4.1340 4.4380 0.0020 ca 1 BEN -0.117000

8 C7 -4.9150 3.2910 0.0000 ca 1 BEN -0.091300

9 C8 -4.7330 5.6920 0.0020 ca 1 BEN -0.129500

10 C9 -6.3030 3.4170 -0.0010 ca 1 BEN -0.117000

11 C10 -6.1130 5.8120 0.0000 ca 1 BEN -0.128000

12 C11 -6.8990 4.6670 -0.0010 ca 1 BEN -0.129500

13 H -0.3230 -1.0350 0.0020 ha 1 BEN 0.155500

14 H1 -0.7890 3.1910 -0.0020 ha 1 BEN 0.155500

15 H2 1.6580 3.4690 -0.0030 ha 1 BEN 0.139500

16 H3 3.1180 1.4870 -0.0010 ha 1 BEN 0.136000

17 H4 2.1330 -0.7700 0.0020 ha 1 BEN 0.139500

18 H5 -3.0690 4.3520 0.0030 ha 1 BEN 0.138500

19 H6 -4.1180 6.5720 0.0030 ha 1 BEN 0.132500

20 H7 -6.5720 6.7820 0.0000 ha 1 BEN 0.132000

21 H8 -7.9690 4.7480 -0.0030 ha 1 BEN 0.132500

22 H9 -6.9190 2.5370 -0.0030 ha 1 BEN 0.138500

23 C12 -2.1650 0.8470 0.0010 c 1 BEN 0.650700

24 O -2.7020 -0.2460 0.0020 o 1 BEN -0.544000

25 O1 -2.8860 1.9840 0.0000 os 1 BEN -0.439900

26 C13 -4.3310 1.9030 0.0000 c3 1 BEN 0.185700

27 H10 -4.6390 1.3460 -0.8730 h1 1 BEN 0.064700

28 H11 -4.6390 1.3460 0.8740 h1 1 BEN 0.064700

@<TRIPOS>BOND

1 1 2 ar

2 1 3 ar

3 1 13 1

4 2 4 ar

5 2 17 1

6 3 5 ar

7 3 23 1

8 4 6 ar

9 4 16 1

10 5 6 ar

11 5 14 1

12 6 15 1

13 7 8 ar

14 7 9 ar

15 7 18 1

16 8 10 ar

17 8 26 1

18 9 11 ar

19 9 19 1

20 10 12 ar

21 10 22 1

22 11 12 ar

23 11 20 1

24 12 21 1

25 23 24 2

26 23 25 1

27 25 26 1

28 26 27 1

29 26 28 1

@<TRIPOS>SUBSTRUCTURE

1 BEN 1 TEMP 0 **** **** 0 ROOT

- **I.2.4 Oleyl Alcohol (oleyl_alcohol.mol2)**

  Flexible long-chain alcohol with unsaturation, optimized and converted via GAMESS and Open Babel.

```
@<TRIPOS>MOLECULE
OLE
  55    54     1     0     0
SMALL
bcc
@<TRIPOS>ATOM
      1 C         -11.3600     0.5380     0.1750 c3        1 OLE      -0.092100
      2 C1        -10.1350    -0.3700     0.0640 c3        1 OLE      -0.080400
      3 C2         -8.8160     0.4050     0.0300 c3        1 OLE      -0.079400
      4 C3         -7.5860    -0.4980    -0.0810 c3        1 OLE      -0.079400
      5 C4         -6.2680     0.2780    -0.1140 c3        1 OLE      -0.079400
      6 C5         -5.0370    -0.6250    -0.2240 c3        1 OLE      -0.079400
      7 C6         -3.7200     0.1510    -0.2570 c3        1 OLE      -0.076400
      8 C7         -2.4880    -0.7580    -0.3610 c3        1 OLE      -0.048200
      9 C8         -1.1980     0.0140    -0.4350 c2        1 OLE      -0.170200
     10 C9         -0.2140    -0.0550     0.4420 c2        1 OLE      -0.171200
     11 C10         1.0760     0.7170     0.3690 c3        1 OLE      -0.048200
     12 C11         2.3080    -0.1920     0.2670 c3        1 OLE      -0.076400
     13 C12         3.6250     0.5840     0.2320 c3        1 OLE      -0.079400
     14 C13         4.8550    -0.3190     0.1250 c3        1 OLE      -0.079400
     15 C14         6.1730     0.4570     0.0880 c3        1 OLE      -0.078400
     16 C15         7.4030    -0.4460    -0.0180 c3        1 OLE      -0.078400
     17 C16         8.7170     0.3360    -0.0560 c3        1 OLE      -0.084400
     18 C17         9.9370    -0.5620    -0.1620 c3        1 OLE       0.131400
```

19	O	11.0800	0.2530	-0.1900	oh	1 OLE -0.601800
20	H	11.8540	-0.2870	-0.2560	ho	1 OLE 0.398000
21	H1	9.8760	-1.1680	-1.0650	h1	1 OLE 0.019700
22	H2	9.9730	-1.2440	0.6860	h1	1 OLE 0.019700
23	H3	8.8170	0.9450	0.8380	hc	1 OLE 0.055700
24	H4	8.7210	1.0200	-0.9010	hc	1 OLE 0.055700
25	H5	7.3190	-1.0610	-0.9130	hc	1 OLE 0.039700
26	H6	7.4150	-1.1360	0.8250	hc	1 OLE 0.039700
27	H7	6.2550	1.0710	0.9840	hc	1 OLE 0.041700
28	H8	6.1620	1.1470	-0.7530	hc	1 OLE 0.041700
29	H9	4.7740	-0.9320	-0.7700	hc	1 OLE 0.039700
30	H10	4.8680	-1.0090	0.9670	hc	1 OLE 0.039700
31	H11	3.7050	1.1980	1.1270	hc	1 OLE 0.040200
32	H12	3.6130	1.2750	-0.6100	hc	1 OLE 0.040200
33	H13	2.2210	-0.8060	-0.6270	hc	1 OLE 0.041700
34	H14	2.3170	-0.8800	1.1100	hc	1 OLE 0.041700
35	H15	1.1720	1.3400	1.2570	hc	1 OLE 0.045700
36	H16	1.0490	1.3920	-0.4830	hc	1 OLE 0.045700
37	H17	-0.3150	-0.7210	1.2880	ha	1 OLE 0.120000
38	H18	-1.0970	0.6790	-1.2810	ha	1 OLE 0.120000
39	H19	-2.5860	-1.3800	-1.2500	hc	1 OLE 0.045700
40	H20	-2.4610	-1.4350	0.4890	hc	1 OLE 0.045700
41	H21	-3.6330	0.7630	0.6380	hc	1 OLE 0.041700
42	H22	-3.7290	0.8410	-1.0990	hc	1 OLE 0.041700
43	H23	-5.1180	-1.2360	-1.1210	hc	1 OLE 0.039700
44	H24	-5.0250	-1.3190	0.6160	hc	1 OLE 0.039700
45	H25	-6.1870	0.8880	0.7840	hc	1 OLE 0.039700

46 H26 -6.2800 0.9720 -0.9530 hc 1 OLE 0.039700

47 H27 -7.6670 -1.1080 -0.9790 hc 1 OLE 0.039700

48 H28 -7.5740 -1.1920 0.7580 hc 1 OLE 0.039700

49 H29 -8.7360 1.0160 0.9270 hc 1 OLE 0.039700

50 H30 -8.8310 1.0990 -0.8090 hc 1 OLE 0.039700

51 H31 -10.2180 -0.9790 -0.8330 hc 1 OLE 0.038700

52 H32 -10.1230 -1.0630 0.9030 hc 1 OLE 0.038700

53 H33 -11.3240 1.1350 1.0820 hc 1 OLE 0.032700

54 H34 -12.2780 -0.0400 0.1960 hc 1 OLE 0.032700

55 H35 -11.4180 1.2210 -0.6670 hc 1 OLE 0.032700

@<TRIPOS>BOND

1 1 2 1

2 1 53 1

3 1 54 1

4 1 55 1

5 2 3 1

6 2 51 1

7 2 52 1

8 3 4 1

9 3 49 1

10 3 50 1

11 4 5 1

12 4 47 1

13 4 48 1

14 5 6 1

15 5 45 1

16 5 46 1

17 6 7 1

18 6 43 1

19 6 44 1

20 7 8 1

21 7 41 1

22 7 42 1

23 8 9 1

24 8 39 1

25 8 40 1

26 9 10 2

27 9 38 1

28 10 11 1

29 10 37 1

30 11 12 1

31 11 35 1

32 11 36 1

33 12 13 1

34 12 33 1

35 12 34 1

36 13 14 1

37 13 31 1

38 13 32 1

39 14 15 1

40 14 29 1

41 14 30 1

42 15 16 1

43 15 27 1

44 15 28 1

45 16 17 1

46 16 25 1

47 16 26 1

48 17 18 1

49 17 23 1

50 17 24 1

51 18 19 1

52 18 21 1

53 18 22 1

54 19 20 1

@<TRIPOS>SUBSTRUCTURE

1 OLE 1 TEMP 0 **** **** 0 ROOT

- **I.2.5 2-Ethyl-1-Hexanol (2-ethyl-1-hexanol. mol2)**

Medium-chain branched alcohol, often used in industrial solvent systems.

@<TRIPOS>MOLECULE

ETH

27 26 1 0 0

SMALL

bcc

@<TRIPOS>ATOM

1 C 3.7680 -1.2350 -0.4000 c3 1 ETH -0.092100

2 C1 2.4900 -1.1240 0.4310 c3 1 ETH -0.080400

3 C2 1.3650 -0.3880 -0.2970 c3 1 ETH -0.079400

4 C3 0.0750 -0.3040 0.5250 c3 1 ETH -0.071400

5 C4 -1.0740 0.4640 -0.1680 c3 1 ETH -0.065700

6 C5 -1.2630 1.8950 0.3630 c3 1 ETH -0.076400

7 C6 -0.0600 2.8210 0.1740 c3 1 ETH -0.092100

8 H 0.8070 2.4790 0.7280 hc 1 ETH 0.035033

9 H1 -0.2940 3.8230 0.5210 hc 1 ETH 0.035033

10 H2 0.2200 2.8910 -0.8730 hc 1 ETH 0.035033

11 H3 -1.5140 1.8520 1.4210 hc 1 ETH 0.037200

12 H4 -2.1200 2.3430 -0.1350 hc 1 ETH 0.037200

13 C7 -2.3920 -0.2950 -0.0420 c3 1 ETH 0.131400

14 O -2.2670 -1.5310 -0.7000 oh 1 ETH -0.600800

15 H5 -3.0580 -2.0370 -0.5790 ho 1 ETH 0.398000

16 H6 -3.1980 0.2860 -0.4850 h1 1 ETH 0.020200

17 H7 -2.6340 -0.4450 1.0110 h1 1 ETH 0.020200

18 H8 -0.8610 0.5220 -1.2340 hc 1 ETH 0.066700

19 H9 0.2880 0.1530 1.4900 hc 1 ETH 0.043700

20 H10 -0.2520 -1.3170 0.7320 hc 1 ETH 0.043700

21 H11 1.1470 -0.8980 -1.2330 hc 1 ETH 0.042200

22 H12 1.7070 0.6090 -0.5660 hc 1 ETH 0.042200

23 H13 2.7120 -0.6130 1.3650 hc 1 ETH 0.037700

24 H14 2.1500 -2.1210 0.7030 hc 1 ETH 0.037700

25 H15 3.5880 -1.7730 -1.3260 hc 1 ETH 0.031700

26 H16 4.5480 -1.7610 0.1420 hc 1 ETH 0.031700

27 H17 4.1530 -0.2520 -0.6600 hc 1 ETH 0.031700

@<TRIPOS>BOND

1 1 2 1

2 1 25 1

3 1 26 1

4 1 27 1

5 2 3 1

6 2 23 1

7 2 24 1

8 3 4 1

9 3 21 1

10 3 22 1

11 4 5 1

12 4 19 1

13 4 20 1

14 5 6 1

15 5 13 1

16 5 18 1

17 6 7 1

18 6 11 1

19 6 12 1

20 7 8 1

21 7 9 1

22 7 10 1

23 13 14 1

24 13 16 1

25 13 17 1

26 14 15 1

@<TRIPOS>SUBSTRUCTURE

1 ETH 1 TEMP 0 **** **** 0 ROOT

- **I.2.6 4-n-Butylphenol (4-n-butylphenol.mol2)**

Phenolic compound with balanced polarity and hydrophobicity for butanol extraction.

@<TRIPOS>MOLECULE

BPH

25 25 1 0 0

SMALL

bcc

@<TRIPOS>ATOM

1	C	-4.5380	0.9010	0.0000	c3	1 BPH -0.093100
2	C1	-3.6200	-0.2860	0.0000	c3	1 BPH -0.080400
3	C2	-2.1950	0.1830	0.0000	c3	1 BPH -0.079400
4	C3	-1.2780	-1.0030	0.0000	c3	1 BPH -0.032100
5	C4	0.0520	-0.5650	0.0000	ca	1 BPH -0.107300
6	C5	0.3270	0.7560	0.0000	ca	1 BPH -0.096500
7	C6	1.6100	1.1780	0.0000	ca	1 BPH -0.181500
8	C7	2.6160	0.2790	0.0000	ca	1 BPH 0.118100
9	C8	2.3410	-1.0430	0.0000	ca	1 BPH -0.181500
10	C9	1.0590	-1.4640	0.0000	ca	1 BPH -0.096500
11	H	0.8550	-2.4440	0.0000	ha	1 BPH 0.134000
12	H1	3.0870	-1.7090	0.0000	ha	1 BPH 0.140500
13	O	3.9460	0.7160	0.0000	oh	1 BPH -0.499100
14	H2	3.9690	1.7160	0.0000	ho	1 BPH 0.418000
15	H3	1.8130	2.1570	0.0000	ha	1 BPH 0.140500
16	H4	-0.4180	1.4220	0.0000	ha	1 BPH 0.134000
17	H5	-1.4460	-1.5560	-0.8160	hc	1 BPH 0.048700
18	H6	-1.4460	-1.5560	0.8160	hc	1 BPH 0.048700
19	H7	-2.0260	0.7350	0.8160	hc	1 BPH 0.042700
20	H8	-2.0260	0.7350	-0.8160	hc	1 BPH 0.042700
21	H9	-3.7900	-0.8390	-0.8160	hc	1 BPH 0.039700

22 H10 -3.7900 -0.8390 0.8160 hc 1 BPH 0.039700

23 H11 -4.3690 1.4540 0.8160 hc 1 BPH 0.033033

24 H12 -5.4880 0.5880 0.0000 hc 1 BPH 0.033033

25 H13 -4.3690 1.4540 -0.8160 hc 1 BPH 0.033033

@<TRIPOS>BOND

1 1 2 1

2 1 23 1

3 1 24 1

4 1 25 1

5 2 3 1

6 2 21 1

7 2 22 1

8 3 4 1

9 3 19 1

10 3 20 1

11 4 5 1

12 4 17 1

13 4 18 1

14 5 6 ar

15 5 10 ar

16 6 7 ar

17 6 16 1

18 7 8 ar

19 7 15 1

20 8 9 ar

21 8 13 1

22 9 10 ar

23 9 12 1

24 10 11 1

25 13 14 1

@<TRIPOS>SUBSTRUCTURE

1 BPH 1 TEMP 0 **** **** 0 ROOT

7. References

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